PATENT ABSTRACTS OF JAPAN

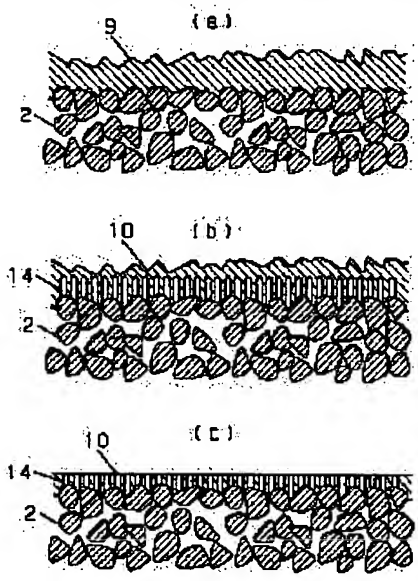
(11)Publication number : **11-049590**
(43)Date of publication of application : **23.02.1999**

(51)Int.Cl. **C04B 41/85**
C04B 38/08
C04B 41/91
H01M 8/02

(21)Application number : **09-207528**
(22)Date of filing : **01.08.1997**

(71)Applicant : **MATSUSHITA ELECTRIC IND CO LTD**
(72)Inventor : **MUKAI YUJI**
TAKAHASHI YASUHITO

(54) **THIN FILM OXYGEN PUMP AND PRODUCTION OF THIN FILM OXYGEN PUMP**



(57)Abstract:
PROBLEM TO BE SOLVED: To obtain an oxygen pump having high oxide ion conductivity by depositing a first electrode having an oxidation-reduction effect, a solid electrolyte thin film having oxide ion conductivity, and a second electrode having oxidation-reduction effect on a porous substrate comprising a porous substrate and a metal oxide layer having a smoothened surface and fine pores on the substrate.
SOLUTION: An aluminum film 9 having about 50 μm thickness is formed by sputtering or the like on an aluminum porous substrate 2 having about 1 μm surface roughness. Then an aluminum 9 formed on the porous substrate 2 is subjected to anodic oxidation in an oxalic acid soln. as an electrolyte by applying a DC voltage from a DC power supply between the aluminum and a Pt counter electrode to form a metal oxide film such as alumina 10 having fine pores 14 of about several 10 nm pore diameter. The surface of the alumina is ground and polished to form a smoothened film. Then a first electrode thin film having an oxidation reduction effect, a solid electrolyte thin film having oxide ion conductivity, and a second electrode thin film having an oxidation-reduction effect are successively deposited on the alumina 10 to obtain a thin film oxygen pump.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to oxygen pumping which used a porosity substrate, its manufacture approach, and a solid electrolyte thin film, and its manufacture approach.
[0002]
[Description of the Prior Art] As oxygen pumping using a solid electrolyte thin film, the oxygen density sensor (1995 for example, Proceedings of the 21 th Chemical Sensor Symposium, 153), the fuel cell (3 (1989) for example, electrochemistry, No. 215), etc. are known.
[0003] Respectively, using a platinum thin film and a zirconia thin film as a redox electrode and an oxygen ion conductivity solid electrolyte, by using a porosity alumina as a substrate, these carry out the laminating of the first platinum-electrode film, a zirconia thin film, and the second platinum-electrode film, and constitute them. The fundamental configuration and actuation of the oxygen-pumping section of this conventional technique are explained using drawing 7 .
[0004] As shown in drawing 7 , on the porosity substrate 2, the thin film oxygen pumping 1 carries out the laminating of the first electrode thin film 3, the solid electrolyte thin film 4 which has oxygen ion conductivity, and the second electrode thin film 5, and is constituted. Thus, it will move to the second electrode thin film 5 side from the first electrode thin film 3 side, and it oxidizes with the second electrode thin film 5, and if direct current voltage is impressed to the constituted thin film oxygen pumping 1 so that DC power supply 6 may be used and the first electrode thin film 3 and the second electrode thin film 5 may become a negative electrical potential difference and a forward electrical potential difference respectively, the negative oxygen ion in the solid electrolyte thin film 4 will serve as oxygen gas, and will be emitted to it. By the first electrode thin film 3 side, it is returned by the first electrode thin film 3 to coincidence to negative oxygen ion, and the oxygen gas which exists in the porosity substrate 2 is supplied into the solid electrolyte thin film 4 with it at it.
[0005] Thereby, oxygen gas moves in the direction of an arrow head 7 to the arrow head 8, and operates as oxygen pumping.
[0006]
[Problem(s) to be Solved by the Invention] In order to improve the engine performance of an oxygen density sensor or a fuel cell, it is necessary to improve the oxygen ion conductivity of a solid electrolyte thin film. The approach of making thickness of a solid electrolyte thin film thin for that purpose is effective.
[0007] On the other hand, since the substrate which forms these devices needs to pass oxygen gas, it is necessary to use a porous material but, and since it is porosity, the surface roughness will become size. However, unless the surface roughness of the substrate ingredient which forms

a thin film is fully smaller than the thickness of the thin film to form, it cannot cover the front face of a substrate completely. This is explained using drawing 8 .
[0008] Although the situation which formed the first electrode thin film 3 on the porosity substrate 2 at drawing 8 (a) is shown, as shown in drawing, the front face of the porosity substrate 2 cannot be covered with the first electrode thin film 3 as the front face of the porosity substrate 2 is uneven. The same is said of the solid electrolyte thin film 4 naturally formed on it, and oxygen pumping cannot be constituted. On the other hand, the porosity substrate 2 needs to supply oxygen without resistance, and high porosity is desired. However, generally, the pore diameter of the porous material with high porosity will also be large, and surface roughness will become large. If thickness of the first electrode thin film 3 is thickened like drawing 8 (b), even if the front face of the porosity substrate 2 is uneven, it is possible to cover the front face. However, since the surface roughness of the first electrode thin film 3 is comparable as the roughness of the porosity substrate 2 of a substrate, unless the solid electrolyte thin film 4 formed on these also thickens the thickness, a front face cannot be covered completely. Therefore, the technical problem that the conductivity of oxygen ion will decrease occurred.
[0009]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the porosity substrate of this invention is characterized by forming the metal oxide layer which has the detailed hole which graduated the front face on a porous substrate.
[0010] Furthermore, the laminating of the thin film oxygen pumping of this invention is carried out in the first electrode which has a oxidation reduction operation on said porosity substrate, the solid electrolyte thin film which has oxygen ion conductivity, and the second electrode which has a oxidation reduction operation.
[0011] Moreover, a primary method is equipped with the process which graduates the front face of said porous layer using the process which forms a wrap metal membrane in a porous substrate front face for the front face of said nature substrate completely, and the process which forms the porous layer which has a detailed hole by anodizing said metal membrane as the manufacture approach of the porosity substrate of this invention.
[0012] The second approach is equipped with the process which forms the porous layer which has a detailed hole, and the process which graduates the front face of said porous layer by countering with cathode and anodizing the field where the process which forms a wrap metal membrane in a porous substrate front face for the front face of said substrate completely and the field in which the metal membrane of said substrate was formed are opposite in an acid solution.
[0013] The third approach is equipped with the process which forms a wrap metal oxide film in a porous substrate front face for the front face of said substrate completely, the process which forms the porous layer which has a detailed hole by returning said metal oxide film, and the process which graduates the front face of said porous layer.
[0014] Furthermore, a primary method is equipped with the process which carries out the laminating of the first electrode which has a oxidation reduction operation, the solid electrolyte thin film which has oxygen ion conductivity, and the second electrode which has a oxidation reduction operation on a porosity substrate with a smooth front face as the manufacture approach of thin film oxygen pumping of this invention.
[0015] The process to which the second approach fills up the inside of the hole of a porosity substrate into a solvent or a specific etching reagent with the solid-state of fusibility, The process which graduates by grinding the front face of the porosity substrate filled up with the solid-state of said fusibility, and forms the first electrode which has a oxidation reduction operation on said

front face which carried out smooth, It has the process which carries out the laminating of the solid electrolyte thin film which has oxygen ion conductivity on said first electrode, and the second electrode which has a oxidation reduction operation to the process eluted with a solvent in the solid-state with which it was filled up in said porosity substrate.
[0016] It has the process which carries out the laminating of the solid electrolyte thin film which has oxygen ion conductivity, and the second electrode which has a oxidation reduction operation on the process which forms the first electrode which has a oxidation reduction operation so that the third approach may furthermore cover the front face of said porosity substrate completely on a porosity substrate front face, the process graduated by grinding the front face of said first electrode, and said first graduated electrode.
[0017]
[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained using drawing 6 from drawing 1 .
[0018] (Gestalt 1 of operation) Drawing 1 is the schematic diagram having shown the approach of smoothing of the porosity substrate by the first example of this invention, and (c) is the process drawing from (a).
[0019] In drawing 1 , 2 is a porosity substrate which consists of an alumina whose surface roughness is about 1 micrometer, and 9 is the aluminum film with a thickness of 50 micrometers formed by the sputtering method on it. Although drawing 1 (a) expresses the condition formed [the front face] thickness for the aluminum film 9 thickly enough completely on the porosity substrate 2 at the wrap sake, the front face is roughness 1 micrometers or more reflecting the surface roughness of the porosity substrate 2.
[0020] Drawing 1 (b) oxidizes the aluminum film 9 using an anode oxidation method, and expresses the condition of having formed the porous alumina 10. The anode oxidation method used here is briefly explained using drawing 2 .
[0021] In this example, 2% of oxalic acid solution 11 was used as the electrolyte, and it anodized by using DC power supply 13 between the counter electrodes 12 which consist of platinum, and impressing an about [20V] electrical potential difference to it by making into an anode plate the aluminum film 9 formed on the porosity substrate 2. Under the present circumstances, oxidation is made to advance by countering with a counter electrode 12 and arranging the porosity substrate 2 side from the field where the aluminum film 9 touches the porosity substrate 2.
[0022] The oxide film on anode of aluminum has the structure where the maximum dense filling of the cel 15 of the shape of a hexagonal prism which has the detailed hole 14 of about 10nm of aperture numbers was carried out as shown in drawing 3 , and a hole 14 is linearly formed in the thickness direction. In addition, drawing 3 (a) is the surface Fig. of an oxidation side, and drawing 3 (b) is a sectional view. Thus, the detailed hole 14 can be formed in high density in an anode oxidation method.
[0023] The alumina 10 shown in drawing 1 (b) is carried out in this way, and is formed, and the detailed hole 14 is formed from the interface with the porosity substrate 2. By carrying out grinding of the front face of this alumina 10, and grinding it, as shown in drawing (c) of drawing 1 , a front face is very smooth, and the porosity substrate which moreover has the detailed hole 14 only on a front face can be obtained.
[0024] If the laminating of the first electrode thin film 3 which has a oxidation reduction operation on this alumina 10, the solid electrolyte thin film 4 which has oxygen ion conductivity, and the second electrode thin film 5 which has a oxidation reduction operation is carried out one by one, the thin film oxygen pumping 1 shown in drawing 7 can be constituted. In this example,

the zirconia was used as platinum and a solid electrolyte which has oxygen ion conductivity as an electrode which has an oxidation reduction operation.
[0025] Since thickness of the solid electrolyte thin film 4 which carries out a laminating by using the technique of this invention can be made thin, good high oxygen pumping of oxygen ion conductivity can be obtained.
[0026] In addition, although this example explained the example using aluminum as a metal porosity-ized with an anode oxidation method, not only direct-current electrolysis but alternating current electrolysis is [that what is necessary is just the metal which does not restrict the technique of this invention to aluminum and is porosity-ized with anode oxidation methods, such as titanium, a tantalum, silicon, niobium, chromium, molybdenum, vanadium, a zirconium, and germanium,] sufficient also as anodic oxidation conditions. Moreover, what is necessary is just to use that to which the electrolytic acid solution also fitted each metal.
[0027] Moreover, in the process to anodize, although oxidation may be made to advance from the aluminum film 9 side, when a hole does not reach even to the porosity substrate 12, it is possible [it] that oxygen permeability falls.
[0028] Like the alumina 10 produced by anodic oxidation of this example, since the smoothing film which has a hole in the thickness direction has the small passage resistance which penetrates a gas to an one direction compared with the porous material with which pore continued like usual three dimensions, it is the the best for thin film oxygen pumping.
[0029] (Gestalt 2 of operation) Drawing 4 is the schematic diagram having shown the approach of smoothing of the porosity substrate by the second example of this invention, and (c) is the process drawing from (a).
[0030] In drawing 4 , 2 is the same porosity substrate as the first example, and 16 is the nickel film formed on it. Drawing 4 (a) expresses the condition formed [the front face] thickness for the nickel film 16 thickly enough completely on the porosity substrate 2 at the wrap sake. In this example, the thickness of this nickel film 16 is about 50 micrometers, and is formed by the sputtering method.
[0031] If this is heated at about 800-900 degrees C in an oxidation furnace, the nickel film 16 will oxidize and it will change to nickel oxide 17. This condition is drawing 4 (b). Next, oxygen is removed out of nickel oxide 17 by heating nickel oxide 17 in a hydrogen ambient atmosphere. The returned nickel is porosity nickel 18 which has a detailed aperture, and by carrying out grinding of the front face, and grinding it, its front face is very smooth and it can obtain the porosity substrate which moreover has a detailed hole.
[0032] By using this substrate, good high oxygen pumping of oxygen ion conductivity which made thickness of a solid electrolyte thin film thin like the first example can be obtained.
[0033] In addition, although this example explained the example using nickel as a metal oxidized and porosity-ized, the technique of this invention is not restricted to this metal. Moreover, nickel oxide may be formed from the beginning.
[0034] (Gestalt 3 of operation) Drawing 5 is the schematic diagram having shown the approach of smoothing of the porosity substrate by the third example of this invention, and (d) is the process drawing from (a).
[0035] In drawing 5 , 2 is the same porosity substrate as the first example. The condition of having heated this porosity substrate 2 with the hot plate, and having fluidized and infiltrated the wax 19 to that pore section is drawing 5 (a). A wax 19 is fluidized at about 200 degrees C from the temperature beyond a room temperature, and should just use what is easily dissolved in solvents, such as alcohol.

[0036] The front face of this porosity substrate 2 is ground and graduated with a wax 19 (drawing 5 (b)), and the first electrode thin film 3 which consists of platinum is formed in that front face (drawing 5 (c)). Since this first electrode thin film 3 is formed at the room temperature using the sputtering method, the wax 19 has maintained that front face, without melting, and can form the small first electrode thin film 3 of surface roughness. Moreover, in case it graduates, the particle on the front face of a substrate has the effectiveness of a pile in dedropping.
[0037] Next, a wax 19 is removed by dipping into alcohol, where this first electrode thin film 3 is formed (drawing 5 (d)). In this way, since the formed first electrode thin film 3 has kept surface roughness small, it can make thickness of a solid electrolyte thin film thin like the above-mentioned example on this, and can obtain good high oxygen pumping of oxygen ion conductivity.
[0038] In addition, in this example, before forming the first electrode thin film 3, it is desirable to irradiate argon ion and oxygen ion in the polished surface which the condition of drawing 5 (b) graduated. This is for the wax component which remained to the field which the porosity substrate 2 ground to be removed by ion irradiation, and for the bond strength of the first electrode thin film 3 to improve by it.
[0039] In addition, although the first electrode thin film 3 was formed by the sputtering method in this example, you may form with a vacuum deposition method, plating, etc.
[0040] Moreover, although the wax was used as an ingredient filled up with this example to the pore section of the porosity substrate 2, low-melt point point metals, such as lead, may instead be used. In this case, as for the metal used for restoration, what can carry out etching removal easily with an acid solution is desirable.
[0041] (Gestalt 4 of operation) Drawing 6 is the schematic diagram having shown the approach of smoothing of the porosity substrate by the fourth example of this invention, and (a) and (b) are the process drawing.
[0042] In drawing 6 , 2 is the same porosity substrate as the first example, and 3 is the first electrode thin film which consists of platinum formed on it. In this example, the thickness of the first electrode thin film 3 is completely formed for the front face thickly enough with about 50 micrometers on the porosity substrate 2 at the wrap sake (drawing 6 (a)). The condition of having deleted about 20 micrometers of front faces of this first electrode thin film 3 by polish, and having graduated them is drawing 6 (b).
[0043] In this way, if the small first electrode thin film 3 of surface roughness is formed, the solid electrolyte thin film of the thin thickness can be carried out like the above-mentioned example on it, and good high oxygen pumping of oxygen ion conductivity can be obtained.
[0044]
[Effect of the Invention] Since thickness of a solid electrolyte thin film can be made thin as mentioned above according to this invention, high oxygen pumping of oxygen ion conductivity can be obtained. Consequently, operating temperature of an oxygen density sensor can be low-temperature-ized, or the output of a fuel cell can be improved.

TECHNICAL FIELD

[Field of the Invention] This invention relates to oxygen pumping which used a porosity substrate, its manufacture approach, and a solid electrolyte thin film, and its manufacture approach.

PRIOR ART

[Description of the Prior Art] As oxygen pumping using a solid electrolyte thin film, the oxygen density sensor (1995 for example, Proceedings of the 21 th Chemical Sensor Symposium, 153), the fuel cell (3 (1989) for example, electrochemistry, No. 215), etc. are known.

[0003] Respectively, using a platinum thin film and a zirconia thin film as a redox electrode and an oxygen ion conductivity solid electrolyte, by using a porosity alumina as a substrate, these carry out the laminating of the first platinum-electrode film, a zirconia thin film, and the second platinum-electrode film, and constitute them. The fundamental configuration and actuation of the oxygen-pumping section of this conventional technique are explained using drawing 7 .

[0004] As shown in drawing 7 , on the porosity substrate 2, the thin film oxygen pumping 1 carries out the laminating of the first electrode thin film 3, the solid electrolyte thin film 4 which has oxygen ion conductivity, and the second electrode thin film 5, and is constituted. Thus, it will move to the second electrode thin film 5 side from the first electrode thin film 3 side, and it oxidizes with the second electrode thin film 5, and if direct current voltage is impressed to the constituted thin film oxygen pumping 1 so that DC power supply 6 may be used and the first electrode thin film 3 and the second electrode thin film 5 may become a negative electrical potential difference and a forward electrical potential difference respectively, the negative oxygen ion in the solid electrolyte thin film 4 will serve as oxygen gas, and will be emitted to it. By the first electrode thin film 3 side, it is returned by the first electrode thin film 3 to coincidence to negative oxygen ion, and the oxygen gas which exists in the porosity substrate 2 is supplied into the solid electrolyte thin film 4 with it at it.

[0005] Thereby, oxygen gas moves in the direction of an arrow head 7 to the arrow head 8, and operates as oxygen pumping.

EFFECT OF THE INVENTION

[Effect of the Invention] Since thickness of a solid electrolyte thin film can be made thin as mentioned above according to this invention, high oxygen pumping of oxygen ion conductivity can be obtained. Consequently, operating temperature of an oxygen density sensor can be low-temperature-ized, or the output of a fuel cell can be improved.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] In order to improve the engine performance of an oxygen density sensor or a fuel cell, it is necessary to improve the oxygen ion conductivity of a solid electrolyte thin film. The approach of making thickness of a solid electrolyte thin film thin for that purpose is effective.

[0007] On the other hand, since the substrate which forms these devices needs to pass oxygen gas, it is necessary to use a porous material but, and since it is porosity, the surface roughness will become size. However, unless the surface roughness of the substrate ingredient which forms a thin film is fully smaller than the thickness of the thin film to form, it cannot cover the front face of a substrate completely. This is explained using drawing 8 .

[0008] Although the situation which formed the first electrode thin film 3 on the porosity substrate 2 at drawing 8 (a) is shown, as shown in drawing, the front face of the porosity substrate 2 cannot be covered with the first electrode thin film 3 as the front face of the porosity

substrate 2 is uneven. The same is said of the solid electrolyte thin film 4 naturally formed on it, and oxygen pumping cannot be constituted. On the other hand, the porosity substrate 2 needs to supply oxygen without resistance, and high porosity is desired. However, generally, the pore diameter of the porous material with high porosity will also be large, and surface roughness will become large. If thickness of the first electrode thin film 3 is thickened like drawing 8 (b), even if the front face of the porosity substrate 2 is uneven, it is possible to cover the front face. However, since the surface roughness of the first electrode thin film 3 is comparable as the roughness of the porosity substrate 2 of a substrate, unless the solid electrolyte thin film 4 formed on these also thickens the thickness, a front face cannot be covered completely. Therefore, the technical problem that the conductivity of oxygen ion will decrease occurred.

MEANS

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the porosity substrate of this invention is characterized by forming the metal oxide layer which has the detailed hole which graduated the front face on a porous substrate.

[0010] Furthermore, the laminating of the thin film oxygen pumping of this invention is carried out in the first electrode which has a oxidation reduction operation on said porosity substrate, the solid electrolyte thin film which has oxygen ion conductivity, and the second electrode which has a oxidation reduction operation.

[0011] Moreover, a primary method is equipped with the process which graduates the front face of said porous layer using the process which forms a wrap metal membrane in a porous substrate front face for the front face of said nature substrate completely, and the process which forms the porous layer which has a detailed hole by anodizing said metal membrane as the manufacture approach of the porosity substrate of this invention.

[0012] The second approach is equipped with the process which forms the porous layer which has a detailed hole, and the process which graduates the front face of said porous layer by countering with cathode and anodizing the field where the process which forms a wrap metal membrane in a porous substrate front face for the front face of said substrate completely and the field in which the metal membrane of said substrate was formed are opposite in an acid solution.

[0013] The third approach is equipped with the process which forms a wrap metal oxide film in a porous substrate front face for the front face of said substrate completely, the process which forms the porous layer which has a detailed hole by returning said metal oxide film, and the process which graduates the front face of said porous layer.

[0014] Furthermore, a primary method is equipped with the process which carries out the laminating of the first electrode which has a oxidation reduction operation, the solid electrolyte thin film which has oxygen ion conductivity, and the second electrode which has a oxidation reduction operation on a porosity substrate with a smooth front face as the manufacture approach of thin film oxygen pumping of this invention.

[0015] The process to which the second approach fills up the inside of the hole of a porosity substrate into a solvent or a specific etching reagent with the solid-state of fusibility, The process which graduates by grinding the front face of the porosity substrate filled up with the solid-state of said fusibility, and forms the first electrode which has a oxidation reduction operation on said front face which carried out smooth, It has the process which carries out the laminating of the solid electrolyte thin film which has oxygen ion conductivity on said first electrode, and the second electrode which has a oxidation reduction operation to the process eluted with a solvent

in the solid-state with which it was filled up in said porosity substrate.
[0016] It has the process which carries out the laminating of the solid electrolyte thin film which has oxygen ion conductivity, and the second electrode which has a oxidation reduction operation on the process which forms the first electrode which has a oxidation reduction operation so that the third approach may furthermore cover the front face of said porosity substrate completely on a porosity substrate front face, the process graduated by grinding the front face of said first electrode, and said first graduated electrode.
[0017]
[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained using drawing 6 from drawing 1 .
[0018] (Gestalt 1 of operation) Drawing 1 is the schematic diagram having shown the approach of smoothing of the porosity substrate by the first example of this invention, and (c) is the process drawing from (a).
[0019] In drawing 1 , 2 is a porosity substrate which consists of an alumina whose surface roughness is about 1 micrometer, and 9 is the aluminum film with a thickness of 50 micrometers formed by the sputtering method on it. Although drawing 1 (a) expresses the condition formed [the front face] thickness for the aluminum film 9 thickly enough completely on the porosity substrate 2 at the wrap sake, the front face is roughness 1 micrometers or more reflecting the surface roughness of the porosity substrate 2.
[0020] Drawing 1 (b) oxidizes the aluminum film 9 using an anode oxidation method, and expresses the condition of having formed the porous alumina 10. The anode oxidation method used here is briefly explained using drawing 2 .
[0021] In this example, 2% of oxalic acid solution 11 was used as the electrolyte, and it anodized by using DC power supply 13 between the counter electrodes 12 which consist of platinum, and impressing an about [20V] electrical potential difference to it by making into an anode plate the aluminum film 9 formed on the porosity substrate 2. Under the present circumstances, oxidation is made to advance by countering with a counter electrode 12 and arranging the porosity substrate 2 side from the field where the aluminum film 9 touches the porosity substrate 2.
[0022] The oxide film on anode of aluminum has the structure where the maximum dense filling of the cel 15 of the shape of a hexagonal prism which has the detailed hole 14 of about 10nm of aperture numbers was carried out as shown in drawing 3 , and a hole 14 is linearly formed in the thickness direction. In addition, drawing 3 (a) is the surface Fig. of an oxidation side, and drawing 3 (b) is a sectional view. Thus, the detailed hole 14 can be formed in high density in an anode oxidation method.
[0023] The alumina 10 shown in drawing 1 (b) is carried out in this way, and is formed, and the detailed hole 14 is formed from the interface with the porosity substrate 2. By carrying out grinding of the front face of this alumina 10, and grinding it, as shown in drawing (c) of drawing 1 , a front face is very smooth, and the porosity substrate which moreover has the detailed hole 14 only on a front face can be obtained.
[0024] If the laminating of the first electrode thin film 3 which has a oxidation reduction operation on this alumina 10, the solid electrolyte thin film 4 which has oxygen ion conductivity, and the second electrode thin film 5 which has a oxidation reduction operation is carried out one by one, the thin film oxygen pumping 1 shown in drawing 7 can be constituted. In this example, the zirconia was used as platinum and a solid electrolyte which has oxygen ion conductivity as an electrode which has an oxidation reduction operation.
[0025] Since thickness of the solid electrolyte thin film 4 which carries out a laminating by using

the technique of this invention can be made thin, good high oxygen pumping of oxygen ion conductivity can be obtained.
[0026] In addition, although this example explained the example using aluminum as a metal porosity-ized with an anode oxidation method, not only direct-current electrolysis but alternating current electrolysis is [that what is necessary is just the metal which does not restrict the technique of this invention to aluminum and is porosity-ized with anode oxidation methods, such as titanium, a tantalum, silicon, niobium, chromium, molybdenum, vanadium, a zirconium, and germanium,] sufficient also as anodic oxidation conditions. Moreover, what is necessary is just to use that to which the electrolytic acid solution also fitted each metal.
[0027] Moreover, in the process to anodize, although oxidation may be made to advance from the aluminum film 9 side, when a hole does not reach even to the porosity substrate 12, it is possible [it] that oxygen permeability falls.
[0028] Like the alumina 10 produced by anodic oxidation of this example, since the smoothing film which has a hole in the thickness direction has the small passage resistance which penetrates a gas to an one direction compared with the porous material with which pore continued like usual three dimensions, it is the the best for thin film oxygen pumping.
[0029] (Gestalt 2 of operation) Drawing 4 is the schematic diagram having shown the approach of smoothing of the porosity substrate by the second example of this invention, and (c) is the process drawing from (a).
[0030] In drawing 4 , 2 is the same porosity substrate as the first example, and 16 is the nickel film formed on it. Drawing 4 (a) expresses the condition formed [the front face] thickness for the nickel film 16 thickly enough completely on the porosity substrate 2 at the wrap sake. In this example, the thickness of this nickel film 16 is about 50 micrometers, and is formed by the sputtering method.
[0031] If this is heated at about 800-900 degrees C in an oxidation furnace, the nickel film 16 will oxidize and it will change to nickel oxide 17. This condition is drawing 4 (b). Next, oxygen is removed out of nickel oxide 17 by heating nickel oxide 17 in a hydrogen ambient atmosphere. The returned nickel is porosity nickel 18 which has a detailed aperture, and by carrying out grinding of the front face, and grinding it, its front face is very smooth and it can obtain the porosity substrate which moreover has a detailed hole.
[0032] By using this substrate, good high oxygen pumping of oxygen ion conductivity which made thickness of a solid electrolyte thin film thin like the first example can be obtained.
[0033] In addition, although this example explained the example using nickel as a metal oxidized and porosity-ized, the technique of this invention is not restricted to this metal. Moreover, nickel oxide may be formed from the beginning.
[0034] (Gestalt 3 of operation) Drawing 5 is the schematic diagram having shown the approach of smoothing of the porosity substrate by the third example of this invention, and (d) is the process drawing from (a).
[0035] In drawing 5 , 2 is the same porosity substrate as the first example. The condition of having heated this porosity substrate 2 with the hot plate, and having fluidized and infiltrated the wax 19 to that pore section is drawing 5 (a). A wax 19 is fluidized at about 200 degrees C from the temperature beyond a room temperature, and should just use what is easily dissolved in solvents, such as alcohol.
[0036] The front face of this porosity substrate 2 is ground and graduated with a wax 19 (drawing 5 </A> (b)), and the first electrode thin film 3 which consists of platinum is formed in that front face (drawing 5 (c)). Since this first electrode thin film 3 is formed at the room

temperature using the sputtering method, the wax 19 has maintained that front face, without melting, and can form the small first electrode thin film 3 of surface roughness. Moreover, in case it graduates, the particle on the front face of a substrate has the effectiveness of a pile in dedropping.

[0037] Next, a wax 19 is removed by dipping into alcohol, where this first electrode thin film 3 is formed (drawing 5 (d)). In this way, since the formed first electrode thin film 3 has kept surface roughness small, it can make thickness of a solid electrolyte thin film thin like the above-mentioned example on this, and can obtain good high oxygen pumping of oxygen ion conductivity.

[0038] In addition, in this example, before forming the first electrode thin film 3, it is desirable to irradiate argon ion and oxygen ion in the polished surface which the condition of drawing 5 (b) graduated. This is for the wax component which remained to the field which the porosity substrate 2 ground to be removed by ion irradiation, and for the bond strength of the first electrode thin film 3 to improve by it.

[0039] In addition, although the first electrode thin film 3 was formed by the sputtering method in this example, you may form with a vacuum deposition method, plating, etc.

[0040] Moreover, although the wax was used as an ingredient filled up with this example to the pore section of the porosity substrate 2, low-melt point point metals, such as lead, may instead be used. In this case, as for the metal used for restoration, what can carry out etching removal easily with an acid solution is desirable.

[0041] (Gestalt 4 of operation) Drawing 6 is the schematic diagram having shown the approach of smoothing of the porosity substrate by the fourth example of this invention, and (a) and (b) are the process drawing.

[0042] In drawing 6 , 2 is the same porosity substrate as the first example, and 3 is the first electrode thin film which consists of platinum formed on it. In this example, the thickness of the first electrode thin film 3 is completely formed for the front face thickly enough with about 50 micrometers on the porosity substrate 2 at the wrap sake (drawing 6 (a)). The condition of having deleted about 20 micrometers of front faces of this first electrode thin film 3 by polish, and having graduated them is drawing 6 (b).

[0043] In this way, if the small first electrode thin film 3 of surface roughness is formed, the solid electrolyte thin film of the thin thickness can be carried out like the above-mentioned example on it, and good high oxygen pumping of oxygen ion conductivity can be obtained.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Process drawing of smoothing of the porosity substrate by the gestalt of the first example of this invention

[Drawing 2] The outline block diagram of an anode oxidation method

[Drawing 3] Structural drawing of an oxide film on anode

[Drawing 4] Process drawing of smoothing of the porosity substrate by the gestalt of the second example of this invention

[Drawing 5] Process drawing of smoothing of the porosity substrate by the gestalt of the third example of this invention

[Drawing 6] Process drawing of smoothing of the porosity substrate by the gestalt of the fourth example of this invention

[Drawing 7] The outline block diagram of thin film oxygen pumping
[Drawing 8] The state diagram of the thin film which formed membranes to up to the porosity substrate
[Description of Notations]
1 Thin Film Oxygen Pumping
2 Porosity Substrate
3 First Electrode Thin Film
4 Solid Electrolyte Thin Film
5 Second Electrode Thin Film
6 DC Power Supply

CLAIMS

[Claim(s)]
[Claim 1] The porosity substrate which comes to form the porous layer which a front face is smooth and has a detailed hole on a porous substrate.
[Claim 2] A porous layer is a porosity substrate according to claim 1 which has the through tube penetrated in the thickness direction of a detailed aperture.
[Claim 3] A porous layer is a porosity substrate according to claim 1 or 2 which consists of a metallic oxide.
[Claim 4] A porous layer is a porosity substrate according to claim 3 which consists of an oxide of the metal porosity-ized with an anode oxidation method.
[Claim 5] The manufacture approach of a porosity substrate of having the process which forms a thin film on a porous substrate, the process which forms the porous layer which has a detailed hole by processing said thin film, and the process which graduates the front face of said porous layer.
[Claim 6] The manufacture approach of a porosity substrate of having the process which forms a metal membrane on a porous substrate, the process which forms the porous layer which has a detailed hole by anodizing said metal membrane, and the process which graduates the front face of said porous layer.
[Claim 7] The manufacture approach of the porosity substrate according to claim 6 characterized by making the field where the field in which the metal membrane was formed is opposite counter with cathode, and anodizing it in an acid solution in the process which forms a porous layer.
[Claim 8] The manufacture approach of a porosity substrate of having the process which forms a metal oxide film on a porous substrate, the process which forms the porous layer which has a detailed hole by returning said metal oxide film, and the process which graduates the front face of said porous layer.
[Claim 9] The process which forms a metal oxide film is the manufacture approach of a porosity substrate according to claim 8 of having the process which forms a metal membrane on a porous substrate, and the process which oxidizes said metal membrane.
[Claim 10] The manufacture approach of a porosity substrate of having the process which fills up the inside of the hole of a porous substrate into a solvent or a specific etching solution with the solid-state of fusibility, the process which graduates the front face of the substrate with which it filled up with the solid-state of said fusibility, and the process eluted with said solvent or a specific etching solution in the solid-state with which it filled up in said substrate.
[Claim 11] Thin film oxygen pumping which comes to carry out the laminating of the 1st

electrode which has a oxidation reduction operation on a porosity substrate given in any of claims 1-4 they are, the solid electrolyte thin film which has oxygen ion conductivity, and the 2nd electrode which has a oxidation reduction operation.

[Claim 12] Thin film oxygen pumping characterized by graduating the front face of said 1st electrode on a porous substrate in thin film oxygen pumping which comes to carry out the laminating of the 1st electrode which has a oxidation reduction operation, the solid electrolyte thin film which has oxygen ion conductivity, and the 2nd electrode which has a oxidation reduction operation.

[Claim 13] The manufacture approach of thin film oxygen pumping which has the process which forms a metal membrane on a porous substrate, the process which forms the porous layer which has a detailed hole by processing said metal membrane, the process which graduates the front face of said porous layer, the 1st electrode which have a oxidation-reduction operation on said graduated porous layer, the solid-electrolyte thin film which have oxygen ion conductivity, and the process which carry out the laminating of the 2nd electrode which has a oxidation-reduction operation.

[Claim 14] The manufacture approach of thin film oxygen pumping according to claim 13 characterized by anodizing a metal membrane in the process which forms a porous layer.

[Claim 15] The manufacture approach of thin film oxygen pumping according to claim 13 characterized by making the field where the field in which the metal membrane was formed is opposite counter with cathode, and anodizing it in an acid solution in the process which forms a porous layer.

[Claim 16] The manufacture approach of thin film oxygen pumping which has the process which forms a metal oxide film on a porous substrate, the process which form the porous layer which has a detailed hole by returning said metal oxide film, the process which graduate the front face of said porous layer, the 1st electrode which have a oxidation-reduction operation on said graduated porous layer, the solid-electrolyte thin film which have oxygen ion conductivity, and the process which carry out the laminating of the 2nd electrode which has a oxidation-reduction operation.

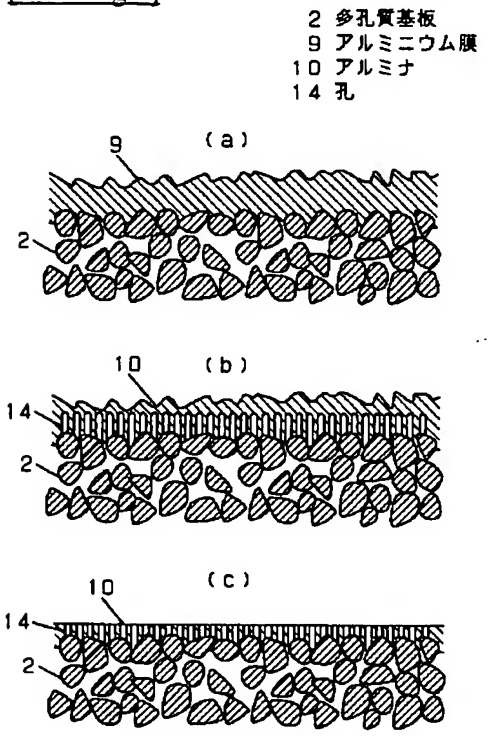
[Claim 17] The process which forms a metal oxide film is the manufacture approach of thin film oxygen pumping according to claim 16 which has the process which forms a metal membrane on a porous substrate, and the process which oxidizes said metal membrane.

[Claim 18] The process which fills up the inside of the hole of a porous substrate into a solvent or a specific etching solution with the solid-state of fusibility, The process which graduates the front face of the substrate with which it filled up with the solid-state of said fusibility, and the 1st electrode which has a oxidation reduction operation on said graduated porous layer, The manufacture approach of thin film oxygen pumping which has the solid electrolyte thin film which has oxygen ion conductivity, the process which carries out the laminating of the 2nd electrode which has a oxidation reduction operation, and the process eluted with said solvent or a specific etching solution in the solid-state with which it filled up in said substrate.

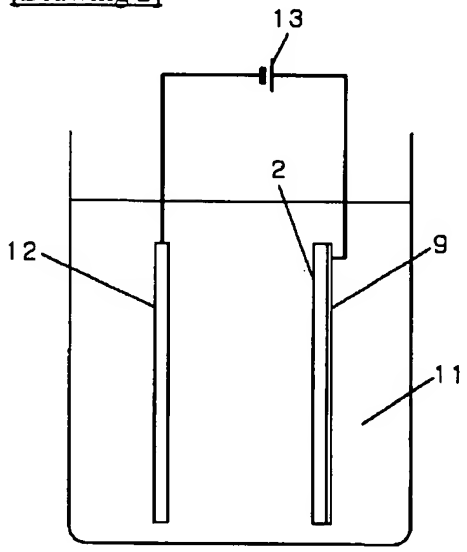
[Claim 19] The manufacture approach of thin film oxygen pumping which has the process which forms the 1st electrode which has a oxidation reduction operation on a porous substrate, the process which graduates the front face of said 1st substrate, the solid electrolyte thin film which has oxygen ion conductivity on said 1st graduated electrode, and the process which carries out the laminating of the 2nd electrode which has a oxidation reduction operation.

DRAWINGS

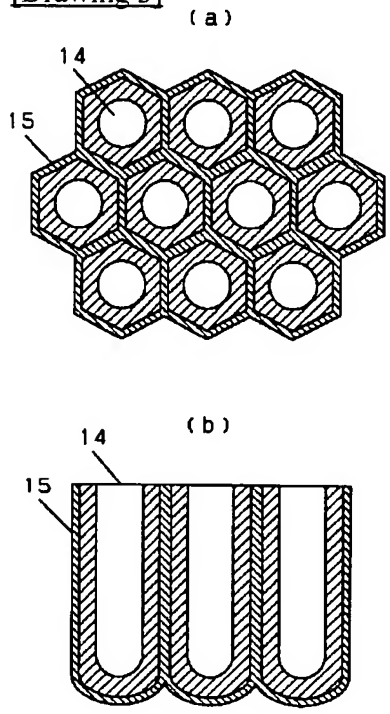
[Drawing 1]



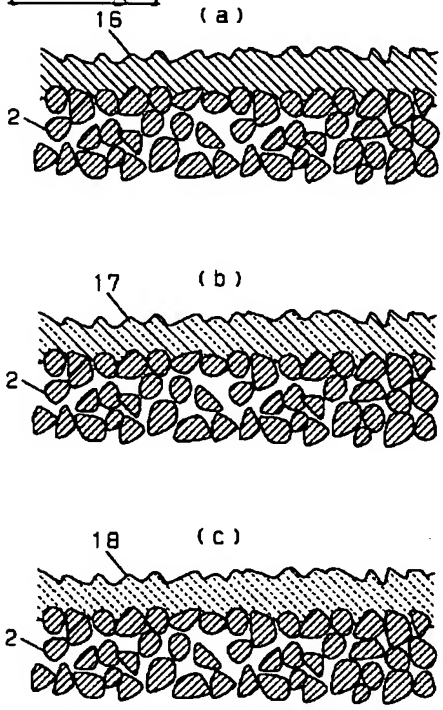
[Drawing 2]



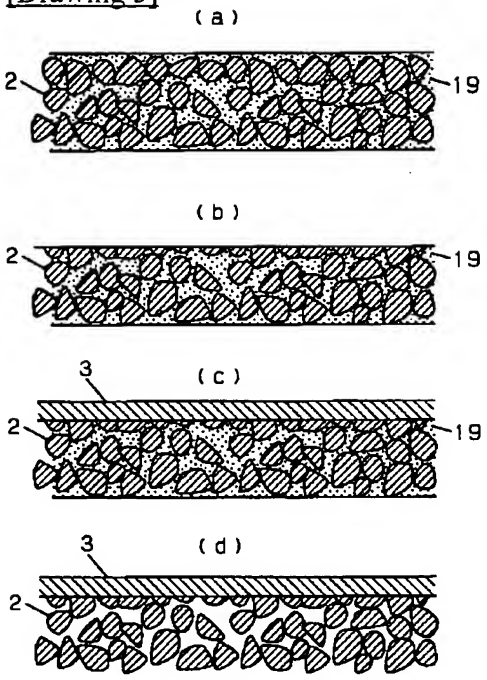
[Drawing 3]



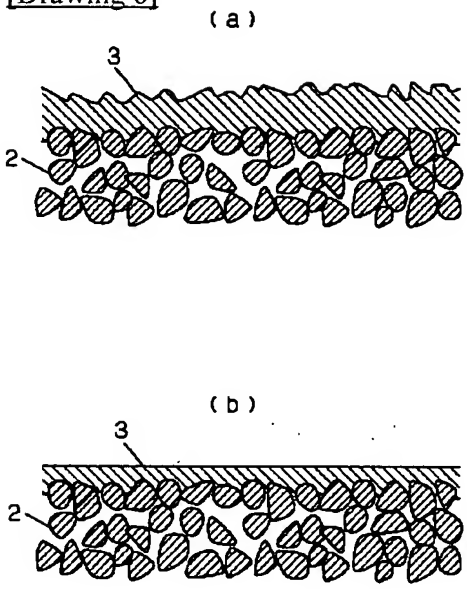
[Drawing 4]



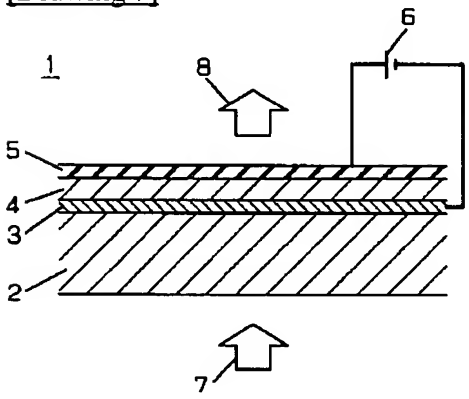
[Drawing 5]



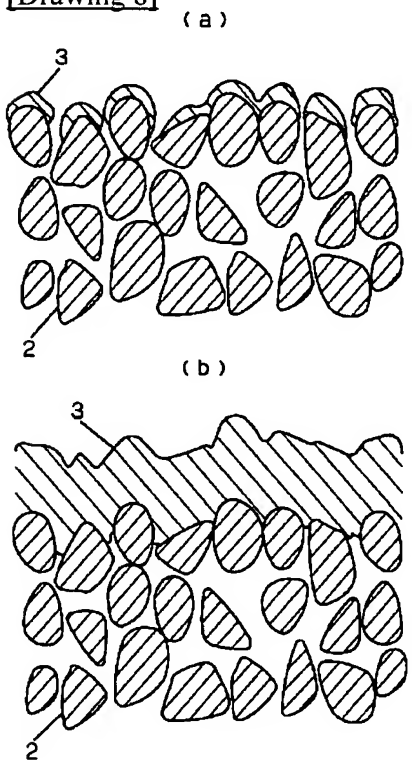
[Drawing 6]



[Drawing 7]



[Drawing 8]



[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（A）　(11)特許出願公開番号

特開平11－49590

(43)公開日　平成11年(1999)２月23日

(51)Int.Cl.⁶	識別記号	ＦＩ	
Ｃ０４Ｂ　41/85		Ｃ０４Ｂ　41/85	Ｃ
38/08		38/08	
41/91		41/91	Ａ
Ｈ０１Ｍ　8/02		Ｈ０１Ｍ　8/02	Ｅ

審査請求　未請求　請求項の数19　ＯＬ　（全７頁）

(21)出願番号　特願平9－207528

(22)出願日　平成９年(1997)８月１日

(71)出願人　000005821
松下電器産業株式会社
大阪府門真市大字門真1006番地

(72)発明者　向井　裕二
大阪府門真市大字門真1006番地　松下電器産業株式会社内

(72)発明者　高橋　康仁
大阪府門真市大字門真1006番地　松下電器産業株式会社内

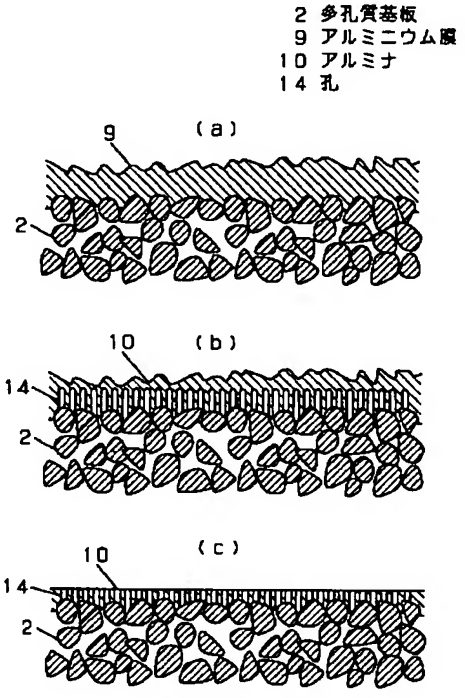
(74)代理人　弁理士　滝本　智之　（外１名）

(54)【発明の名称】　薄膜酸素ポンプおよび薄膜酸素ポンプの製造方法

(57)【要約】

【課題】　薄膜酸素ポンプを形成する基板は酸素ガスを通過する必要があるため、多孔質材料を用いる必要があるが、多孔質であるためにその表面荒さが大となってしまう。そのために固体電解質膜を薄くすることができず、酸素イオンの伝導度を向上することができなかった。

【解決手段】　多孔質基板の表面に、それを覆うに十分な厚さの金属膜を形成し、その金属膜を酸化、あるいは酸化して再び還元することにより、微細な孔径を有する多孔質層を形成し、その表面を平滑化して用いる。



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【特許請求の範囲】

【請求項１】　多孔質の基板上に、表面が平滑で、微細な孔を有する多孔質層を形成してなる多孔質基板。

【請求項２】　多孔質層は、微細な孔径の、厚さ方向に貫通した貫通孔を有する請求項１記載の多孔質基板。

【請求項３】　多孔質層は、金属酸化物からなる請求項１または２記載の多孔質基板。

【請求項４】　多孔質層は、陽極酸化法により多孔質化する金属の酸化物からなる請求項３記載の多孔質基板。

【請求項５】　多孔質の基板上に薄膜を形成する工程と、

前記薄膜を処理することで、微細な孔を有する多孔質層を形成する工程と、

前記多孔質層の表面を平滑化する工程とを有する多孔質基板の製造方法。

【請求項６】　多孔質の基板上に金属膜を形成する工程と、

前記金属膜を陽極酸化することで、微細な孔を有する多孔質層を形成する工程と、

前記多孔質層の表面を平滑化する工程とを有する多孔質基板の製造方法。

【請求項７】　多孔質層を形成する工程において、金属膜を形成した面の反対の面を、酸溶液中で陰極と対向させて陽極酸化することを特徴とする請求項６記載の多孔質基板の製造方法。

【請求項８】　多孔質の基板上に金属酸化膜を形成する工程と、

前記金属酸化膜を還元することで微細な孔を有する多孔質層を形成する工程と、

前記多孔質層の表面を平滑化する工程とを有する多孔質基板の製造方法。

【請求項９】　金属酸化膜を形成する工程は、

多孔質の基板上に金属膜を形成する工程と、前記金属膜を酸化する工程とを有する請求項８記載の多孔質基板の製造方法。

【請求項１０】　多孔質の基板の孔内を、溶媒または特定のエッチング溶液に可溶性の固体で充填する工程と、

前記可溶性の固体が充填された基板の表面を平滑化する工程と、

前記基板内に充填された固体を、前記溶媒または特定のエッチング溶液で溶出する工程とを有する多孔質基板の製造方法。

【請求項１１】　請求項１～４の何れかに記載の多孔質基板上に、

酸化還元作用を有する第１の電極と、酸素イオン伝導性を有する固体電解質薄膜と、酸化還元作用を有する第２の電極とを積層してなる薄膜酸素ポンプ。

【請求項１２】　多孔質の基板上に、酸化還元作用を有する第１の電極と、酸素イオン伝導性を有する固体電解質薄膜と、酸化還元作用を有する第２の電極とを積層してなる薄膜酸素ポンプにおいて、

前記第１の電極の表面が平滑化されていることを特徴とする薄膜酸素ポンプ。

【請求項１３】　多孔質の基板上に金属膜を形成する工程と、

前記金属膜を処理することで、微細な孔を有する多孔質層を形成する工程と、前記多孔質層の表面を平滑化する工程と、

前記平滑化した多孔質層上に、酸化還元作用を有する第１の電極と、酸素イオン伝導性を有する固体電解質薄膜と、酸化還元作用を有する第２の電極を積層する工程とを有する薄膜酸素ポンプの製造方法。

【請求項１４】　多孔質層を形成する工程において、金属膜を陽極酸化することを特徴とする請求項１３記載の薄膜酸素ポンプの製造方法。

【請求項１５】　多孔質層を形成する工程において、金属膜を形成した面の反対の面を、酸溶液中で陰極と対向させて陽極酸化することを特徴とする請求項１３記載の薄膜酸素ポンプの製造方法。

【請求項１６】　多孔質の基板上に金属酸化膜を形成する工程と、

前記金属酸化膜を還元することで微細な孔を有する多孔質層を形成する工程と、前記多孔質層の表面を平滑化する工程と、

前記平滑化した多孔質層上に、酸化還元作用を有する第１の電極と、酸素イオン伝導性を有する固体電解質薄膜と、酸化還元作用を有する第２の電極を積層する工程とを有する薄膜酸素ポンプの製造方法。

【請求項１７】　金属酸化膜を形成する工程は、

多孔質の基板上に金属膜を形成する工程と、前記金属膜を酸化する工程とを有する請求項１６記載の薄膜酸素ポンプの製造方法。

【請求項１８】　多孔質の基板の孔内を、溶媒または特定のエッチング溶液に可溶性の固体で充填する工程と、

前記可溶性の固体が充填された基板の表面を平滑化する工程と、

前記平滑化した多孔質層上に、酸化還元作用を有する第１の電極と、酸素イオン伝導性を有する固体電解質薄膜と、酸化還元作用を有する第２の電極を積層する工程と、

前記基板内に充填された固体を、前記溶媒または特定のエッチング溶液で溶出する工程とを有する薄膜酸素ポンプの製造方法。

【請求項１９】　多孔質の基板上に、酸化還元作用を有する第１の電極を形成する工程と、

前記第１の基板の表面を平滑化する工程と、

前記平滑化した第１の電極上に、酸素イオン伝導性を有する固体電解質薄膜と、酸化還元作用を有する第２の電極を積層する工程とを有する薄膜酸素ポンプの製造方法。

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【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、多孔質基板およびその製造方法、ならびに固体電解質薄膜を用いた酸素ポンプおよびその製造方法に関する。

【０００２】

【従来の技術】固体電解質薄膜を用いた酸素ポンプとしては、酸素濃度センサー（例えば、Proceedings of the 21th Chemical Sensor Symposium、1995、153）や燃料電池（例えば、電気化学、No.3(1989)、215）などが知られている。

【０００３】これらは、酸化還元電極および酸素イオン伝導性固体電解質として、各々白金薄膜とジルコニア薄膜を用い、多孔質アルミナを基板として、第一の白金電極膜とジルコニア薄膜と第二の白金電極膜を積層して構成している。この従来技術の酸素ポンプ部の基本的な構成と動作を図７を用いて説明する。

【０００４】図７に示すように、薄膜酸素ポンプ１は、多孔質基板２上に第一電極薄膜３と酸素イオン伝導性を有する固体電解質薄膜４と第二電極薄膜５を積層して構成される。このように構成された薄膜酸素ポンプ１に、直流電源６を用いて第一電極薄膜３と第二電極薄膜５が各々負電圧と正電圧になるように直流電圧を印加すると、固体電解質薄膜４内の負の酸素イオンが第一電極薄膜３側から第二電極薄膜５側へと移動し、第二電極薄膜５によって酸化され酸素ガスとなって放出される。同時に第一電極薄膜３側では多孔質基板２内に存在する酸素ガスが第一電極薄膜３によって負の酸素イオンへ還元され固体電解質薄膜４内へ供給される。

【０００５】これにより、酸素ガスは矢印７から矢印８の方向へ移動し、酸素ポンプとして動作する。

【０００６】

【発明が解決しようとする課題】酸素濃度センサーや燃料電池の性能を向上するには、固体電解質薄膜の酸素イオン伝導性を向上する必要がある。そのためには固体電解質薄膜の膜厚を薄くする方法が有効である。

【０００７】一方、これらのデバイスを形成する基板は酸素ガスを通過する必要があるため、多孔質材料を用いる必要があるが、多孔質であるためにその表面荒さが大となってしまう。しかし、薄膜を形成する基板材料の表面荒さは、形成する薄膜の厚さより十分に小さくないと基板の表面を完全に覆うことができない。このことを図８を用いて説明する。

【０００８】図８（ａ）に多孔質基板２上に第一電極薄膜３を形成した状況を示しているが、図のように多孔質基板２の表面が凸凹であると多孔質基板２の表面を第一電極薄膜３で覆うことができない。当然その上に形成する固体電解質薄膜４も同様であり、酸素ポンプを構成することができない。一方、多孔質基板２は抵抗無く酸素を供給する必要があり、高い気孔率が望まれる。しかし、一般的に気孔率の高い多孔質材料は気孔径も大きく、表面の荒さが大きくなってしまう。図８（ｂ）のように第一電極薄膜３の膜厚を厚くすれば多孔質基板２の表面が凸凹であってもその表面を覆うことは可能である。しかし第一電極薄膜３の表面荒さは下地の多孔質基板２の荒さと同程度であるため、これらの上に形成する固体電解質薄膜４もその膜厚を厚くしないと表面を完全に覆うことができない。そのために酸素イオンの伝導度が減少してしまうという課題があった。

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【０００９】

【課題を解決するための手段】上記課題を解決するため本発明の多孔質基板は、多孔質の基板上に、表面を平滑化した微細な孔を有する金属酸化物層が形成されたことを特徴とする。

【００１０】さらに、本発明の薄膜酸素ポンプは、前記多孔質基板上に、酸化還元作用を有する第一電極と、酸素イオン伝導性を有する固体電解質薄膜と、酸化還元作用を有する第二電極を積層されたものである。

【００１１】また、本発明の多孔質基板の製造方法として、第一の方法は、多孔質の基板表面に、前記質基板の表面を完全に覆う金属膜を形成する工程と、前記金属膜を陽極酸化することによって微細な孔を有する多孔質層を形成する工程を用いて前記多孔質層の表面を平滑化する工程とを備える。

【００１２】第二の方法は、多孔質の基板表面に、前記基板の表面を完全に覆う金属膜を形成する工程と、前記基板の金属膜を形成した面の反対の面を酸溶液中で陰極と対向して陽極酸化することによって微細な孔を有する多孔質層を形成する工程と、前記多孔質層の表面を平滑化する工程とを備える。

【００１３】第三の方法は、多孔質の基板表面に、前記基板の表面を完全に覆う金属酸化膜を形成する工程と、前記金属酸化膜を還元することによって微細な孔を有する多孔質層を形成する工程と、前記多孔質層の表面を平滑化する工程とを備える。

【００１４】さらに、本発明の薄膜酸素ポンプの製造方法として、第一の方法は、表面が平滑な多孔質基板上に、酸化還元作用を有する第一電極と酸素イオン伝導性を有する固体電解質薄膜と酸化還元作用を有する第二電極を積層する工程を備える。

【００１５】第二の方法は、多孔質基板の孔内を溶媒または特定のエッチング液に可溶性の固体で充填する工程と、前記可溶性の固体で充填された多孔質基板の表面を研磨することによって平滑化し、前記平滑した表面上に酸化還元作用を有する第一電極を形成する工程と、前記多孔質基板内に充填した固体を溶媒で溶出する工程と、前記第一電極上に酸素イオン伝導性を有する固体電解質薄膜と酸化還元作用を有する第二電極を積層する工程とを備える。

【００１６】更に第三の方法は、多孔質基板表面に、前

記多孔質基板の表面を完全に覆うように酸化還元作用を有する第一電極を形成する工程と、前記第一電極の表面を研磨することによって平滑化する工程と、前記平滑化した第一電極上に酸素イオン伝導性を有する固体電解質薄膜と酸化還元作用を有する第二電極を積層する工程とを備える。

【００１７】

【発明の実施の形態】以下、本発明の実施の形態について、図１から図６を用いて説明する。

【００１８】（実施の形態１）図１は本発明の第一の実施例による多孔質基板の平滑化の方法を示した概略図であり、（ａ）から（ｃ）はその工程図である。

【００１９】図１において、２は表面荒さが約１μｍ程度のアルミナからなる多孔質基板であり、９はその上にスパッタリング法で形成した厚さ５０μｍのアルミニウム膜である。図１（ａ）は多孔質基板２上にその表面を完全に覆うためにアルミニウム膜９を膜厚を十分に厚く形成した状態を表しているが、その表面は多孔質基板２の表面荒さを反映して１μｍ以上の荒さになっている。

【００２０】図１（ｂ）は陽極酸化法を用いてアルミニウム膜９を酸化し、多孔質のアルミナ１０を形成した状態を表している。ここで用いた陽極酸化法を図２を用いて簡単に説明する。

【００２１】本実施例では２％のシュウ酸溶液１１を電解質とし、多孔質基板２上に形成したアルミニウム膜９を陽極として、白金からなる対極１２との間に直流電源１３を用いて２０Ｖ程度の電圧を印加することによって陽極酸化を行った。この際、多孔質基板２側を対極１２と対向して配置することにより、アルミニウム膜９は多孔質基板２に接する面から酸化が進行するようにしている。

【００２２】アルミニウムの陽極酸化膜は図３に示したように、孔径数十ｎｍ程度の微細な孔１４を有する六角柱状のセル１５が最密充てんされた構造を持ち、孔１４は厚さ方向に直線的に形成される。なお、図３（ａ）は酸化面の表面図であり、図３（ｂ）は断面図である。このように、陽極酸化法では微細な孔１４を高密度に形成することができる。

【００２３】図１（ｂ）に示したアルミナ１０はこのようにして形成したものであり、多孔質基板２との界面から微細な孔１４が形成されている。このアルミナ１０の表面を研削し研磨することによって、図１の図（ｃ）に示したように表面が極めて平滑で、しかも表面にのみ微細な孔１４を有する多孔質な基板を得ることができる。

【００２４】このアルミナ１０の上に、酸化還元作用を有する第一電極薄膜３と、酸素イオン伝導性を有する固体電解質薄膜４と、酸化還元作用を有する第二電極薄膜５を順次積層すれば、図７に示した薄膜酸素ポンプ１を構成することができる。本実施例では、酸化還元作用を有する電極として白金、酸素イオン伝導性を有する固体電解質としてジルコニアを用いた。

【００２５】本発明の技術を用いることにより、積層する固体電解質薄膜４の厚さを薄くすることができるため、酸素イオン伝導性の高い良好な酸素ポンプを得ることができる。

【００２６】なお、本実施例では陽極酸化法により多孔質化する金属としてアルミニウムを用いた例を説明したが、本発明の技術はアルミニウムに限るものではなく、チタン、タンタル、シリコン、ニオブ、クロム、モリブデン、バナジウム、ジルコニウム、ゲルマニウムなどの陽極酸化法によって多孔質化する金属であれば良く、陽極酸化条件も直流電解に限らず交流電解でも良い。また、電解質の酸溶液も各金属に適したものを用いれば良い。

【００２７】また、陽極酸化する工程において、アルミニウム膜９側から酸化が進行するようにしてもよいが、孔が多孔質基板１２まで到達しない場合には酸素透過性が低下することが考えられる。

【００２８】本実施例の陽極酸化で作製したアルミナ１０のように、厚さ方向に孔を有する平滑化膜は、通常の三次元的に気孔が連続した多孔質材料に比べ、一方向に気体を透過する通過抵抗が小さいため、薄膜酸素ポンプに最適である。

【００２９】（実施の形態２）図４は本発明の第二の実施例による多孔質基板の平滑化の方法を示した概略図であり、（ａ）から（ｃ）はその工程図である。

【００３０】図４において、２は第一の実施例と同じ多孔質基板であり、１６はその上に形成したニッケル膜である。図４（ａ）は多孔質基板２上にその表面を完全に覆うためにニッケル膜１６を膜厚を十分に厚く形成した状態を表している。本実施例では、このニッケル膜１６の膜厚は約５０μｍであり、スパッタリング法により形成している。

【００３１】これを酸化炉内で８００～９００℃程度に加熱するとニッケル膜１６が酸化され酸化ニッケル１７へ変化する。この状態が図４（ｂ）である。次に、酸化ニッケル１７を水素雰囲気中で加熱することによって酸化ニッケル１７中から酸素を取り除く。還元されたニッケルは微細な孔径を有する多孔質ニッケル１８であり、その表面を研削し研磨することによって、表面が極めて平滑で、しかも微細な孔を有する多孔質な基板を得ることができる。

【００３２】この基板を用いることにより、第一の実施例と同様にして固体電解質薄膜の厚さを薄くした酸素イオン伝導性の高い良好な酸素ポンプを得ることができる。

【００３３】なお、本実施例では酸化して多孔質化する金属としてニッケルを用いた例を説明したが、本発明の技術はこの金属に限るものではない。また、最初から酸化ニッケルを形成してもよい。

【００３４】（実施の形態３）図５は本発明の第三の実施例による多孔質基板の平滑化の方法を示した概略図であり、（ａ）から（ｄ）はその工程図である。

【００３５】図５において、２は第一の実施例と同じ多孔質基板である。この多孔質基板２をホットプレートで加熱し、その気孔部へワックス１９を流動化してしみ込ませた状態が図５（ａ）である。ワックス１９は室温以上の温度から２００℃程度で流動化し、アルコールなどの溶剤に容易に溶解するものを用いれば良い。

【００３６】この多孔質基板２の表面をワックス１９と共に研磨して平滑化し（図５（ｂ））、その表面に白金からなる第一電極薄膜３を形成する（図５（ｃ））。この第一電極薄膜３はスパッタリング法を用いて室温で形成しているため、ワックス１９は溶けることなくその表面を保ったままであり、表面荒さの小さな第一電極薄膜３を形成することができる。また、平滑化する際に基板表面の粒子が脱落しにくいという効果もある。

【００３７】次に、この第一電極薄膜３を形成した状態でアルコール中に浸すことによりワックス１９を除去する（図５（ｄ））。こうして形成した第一電極薄膜３は表面荒さを小さく保ったままであるため、この上に前述の実施例と同様にして固体電解質薄膜の厚さを薄くすることができ、酸素イオン伝導性の高い良好な酸素ポンプを得ることができる。

【００３８】なお、本実施例では第一電極薄膜３を形成する前に、図５（ｂ）の状態の平滑化した研磨面に、アルゴンイオンや酸素イオンを照射することが望ましい。これはイオン照射によって多孔質基板２の研磨した面に残留したワックス成分が除去され、第一電極薄膜３の付着強度が向上されるためである。

【００３９】なお、本実施例では第一電極薄膜３をスパッタリング法で形成したが、真空蒸着法やメッキ法などで形成しても良い。

【００４０】また、本実施例では多孔質基板２の気孔部へ充填する材料としてワックスを用いたが、この代わりに鉛などの低融点金属を用いても良い。この場合、充填に用いる金属は酸溶液により容易にエッチング除去できるものが望ましい。

【００４１】（実施の形態４）図６は本発明の第四の実施例による多孔質基板の平滑化の方法を示した概略図であり、（ａ）と（ｂ）はその工程図である。

【００４２】図６において、２は第一の実施例と同じ多孔質基板であり、３はその上に形成した白金からなる第一電極薄膜である。本実施例では多孔質基板２上にその表面を完全に覆うために第一電極薄膜３の膜厚を約５０μｍと十分に厚く形成している（図６（ａ））。この第一電極薄膜３の表面を研磨により約２０μｍ程度削り、平滑化した状態が図６（ｂ）である。

【００４３】こうして表面荒さの小さな第一電極薄膜３を形成しておくとその上に前述の実施例と同様に薄い膜厚の固体電解質薄膜することができ、酸素イオン伝導性の高い良好な酸素ポンプを得ることができる。

【００４４】

【発明の効果】以上のように本発明によれば、固体電解質薄膜の厚さを薄くすることができるため、酸素イオン伝導性の高い酸素ポンプを得ることができる。その結果、酸素濃度センサーの動作温度を低温化したり、燃料電池の出力を向上することができる。

【図面の簡単な説明】

【図１】本発明の第一の実施例の形態による多孔質基板の平滑化の工程図

【図２】陽極酸化法の概略構成図

【図３】陽極酸化膜の構造図

【図４】本発明の第二の実施例の形態による多孔質基板の平滑化の工程図

【図５】本発明の第三の実施例の形態による多孔質基板の平滑化の工程図

【図６】本発明の第四の実施例の形態による多孔質基板の平滑化の工程図

【図７】薄膜酸素ポンプの概略構成図

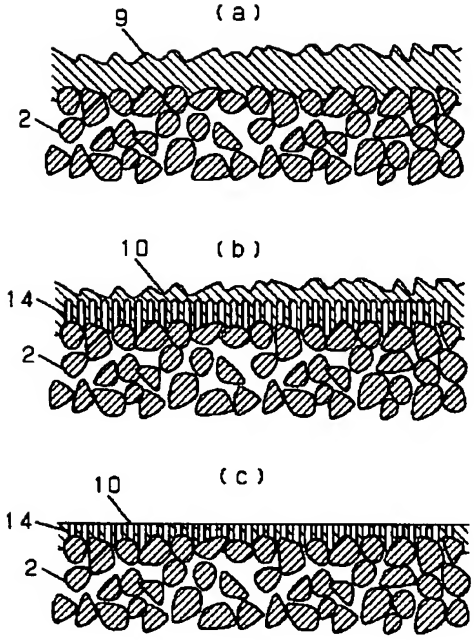
【図８】多孔質基板上へ成膜した薄膜の状態図

【符号の説明】

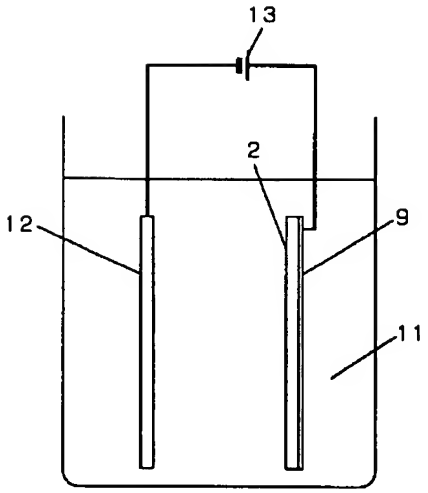
1　薄膜酸素ポンプ
2　多孔質基板
3　第一電極薄膜
4　固体電解質薄膜
5　第二電極薄膜
6　直流電源

【図１】

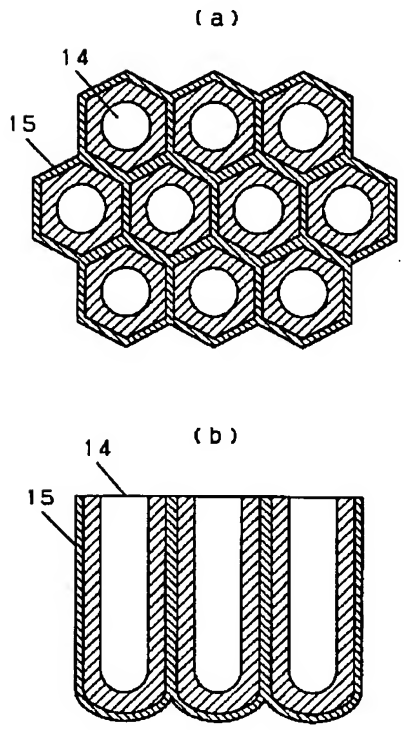
２ 多孔質基板
９ アルミニウム膜
１０ アルミナ
１４ 孔



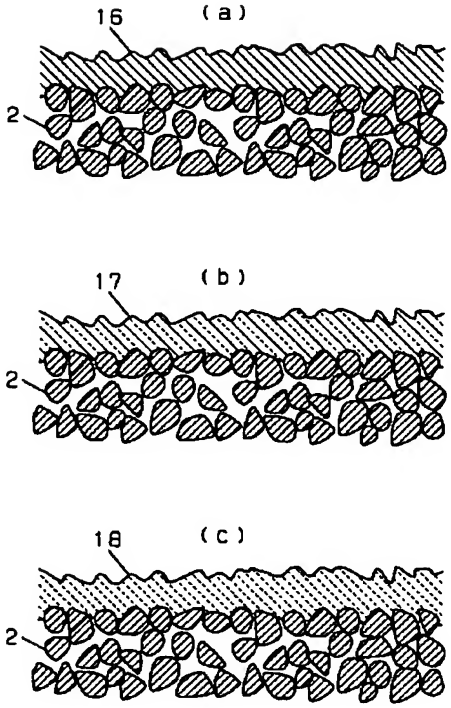
【図２】



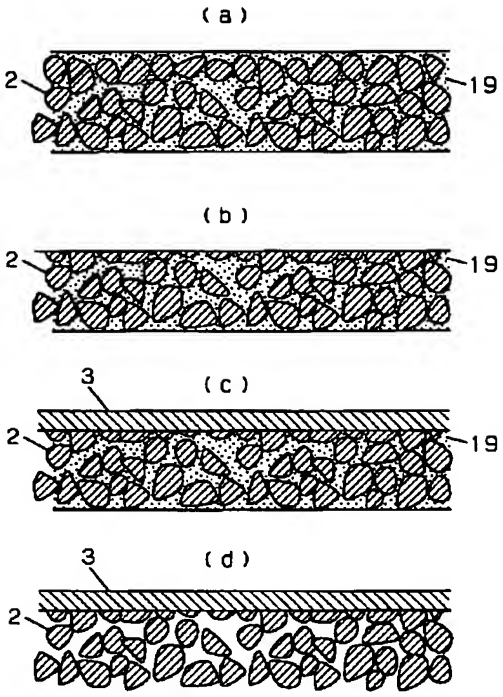
【図３】



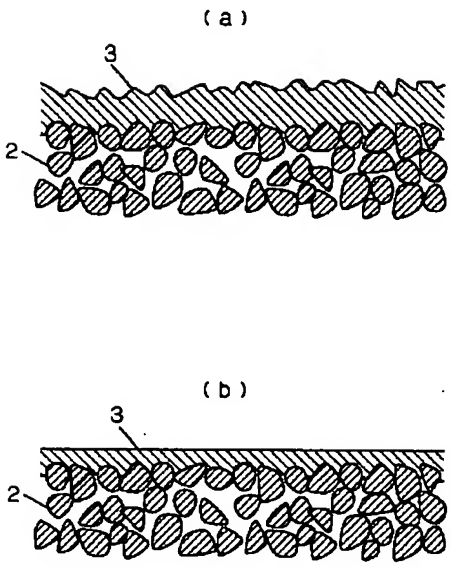
【図４】



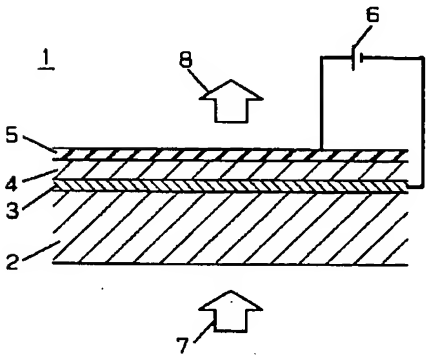
【図５】



【図６】



【図７】



【図８】